

PTO 2010-3468

Japanese Kokai Patent Publication No. 2003-268353, published September 25, 2003;  
Application No. 2002-76392, filed March 19, 2002; Inventors: Keiji OTA, Shinichi  
HABA, Keiji FUKUDA, and Kazunori ITO; Assignee: Rodel Nitta Co.

---

PREPARATION METHOD OF FUMED SILICA AQUEOUS DISPERSION

---

(54) [Title of Invention] Title of Invention:

Preparation Method of Fumed Silica Aqueous Dispersion

[Claims]

[Claim 1] A preparation method of fumed silica aqueous dispersion characterized in that fumed silica is added into a liquid in which pH is 2 – 11 while applying shear force, and an intermediate aqueous dispersion is formed in which said silica concentration is about 20 – 60 % by weight, and, by adding said intermediate aqueous dispersion into a basic liquid, it is adjusted such that the resulting silica concentration is 1 – 50% by weight while pH is about 8 – 12.

[Claim 2] The preparation method of fumed silica aqueous dispersion of Claim 1 characterized in that the resulting silica concentration is 10 - 30 % by weight.

[Claim 3] The preparation method of fumed silica aqueous dispersion of Claim 1 characterized in that the resulting silica concentration is 11 - 13 % by weight.

[Claim 4] The preparation method of fumed silica aqueous dispersion described in any of the Claims 1 – 3 characterized in that after said intermediate aqueous dispersion has been added into the basic liquid, it is passed through a filter with mesh size of about 30  $\mu$ m or less.

[Claim 5] The preparation method of fumed silica aqueous dispersion described in any of the Claims 1 – 4 characterized in that the fumed silica added has a specific surface area of about 40 – 300 sq. m /g.

[Detailed Explanation of Invention]

[0001]

[Field of Invention] This invention pertains to a preparation method of fumed silica aqueous dispersion that can be used as polishing slurry in the manufacture process of semiconductor and electronic parts.

[0002]

[Prior Art] In Prior Art are known fumed silica particles are known that are synthesized by means of a vapor phase hydrolysis reaction (fumed method) using silicon tetrachloride, hydrogen, and oxygen as raw materials in a high temperature flame.

[0003] Said fumed silica is a high grade raw material with very few impurities, and is used for various purposes, for example, it is used also as the abrasive grains of aqueous

dispersion (semiconductor wafer polishing slurry), which is a polishing agent for the semiconductor industry. In the aqueous dispersion of this fumed silica dry type powder is first dispersed in pure water (or pure water including a chemical), and is then formed by adding a basic liquid into this silica dispersion and adjusting pH to basicity.

[0004] However, when this aqueous dispersion is sitting still the fumed silica maintains a good state of dispersion, but when continuous energy is applied, the dispersion state becomes unstable and condensation ensues, which is a problem.

[0005]

[Problems to be Solved by Invention] Therefore, this invention has been made to offer a preparation method of fumed silica aqueous dispersion that does not condense as readily as that of Prior Art.

[0006] Means of Solving the Problem] The following technical means are provided to solve this problem.

[0007] ① The preparation method of fumed silica aqueous dispersion of this invention is characterized in that fumed silica is added into a liquid in which pH is 2 – 11 while applying shear force, and an intermediate aqueous dispersion is formed in which said silica concentration is about 20 – 60 % by weight, and, by adding said intermediate aqueous dispersion into a basic liquid, it is adjusted such that the resulting silica concentration is 1 – 50% by weight while pH is about 8 – 12.

[0008] In this preparation method, since the fumed silica intermediate aqueous dispersion is added into a basic liquid, the fumed silica is dispersed in the basic liquid in small amounts, and the silica concentration in basic liquid (it becomes the "receiving matrix") increases gradually from zero; therefore the silica particles in the intermediate aqueous dispersion being added can quickly shift to the alkaline region where the zeta potential turns high and the dispersion state turns stable; the stability can be higher with regard to the condensation of the dispersion. Moreover, by means of this method, when the intermediate aqueous dispersion is added, condensation does not arise readily even if the intermediate aqueous suspension is gently stirred.

[0009] Moreover, in a method where the basic liquid is added into the fumed silica intermediate aqueous dispersion, as was the case in Prior Art, the silica particles of the fumed silica intermediate aqueous dispersion (the receiving matrix) shift from the acidic region where the zeta potential is low and the dispersion state is unstable via a neutral region to the alkaline region, and they condense extremely readily if there is no stirring that would apply full shearing force during the adding of the basic liquid.

[0010] ② The resulting silica concentration can be made about 10 – 30 % by weight.

[0011] When the resulting silica concentration is made about 10 – 30 % by weight, preferably 10 – 20 % by weight, it is possible to further increase stability with regard to condensation.

[0012] ③ The resulting silica concentration can be made about 11 – 13 % by weight.

[0013] With such constitution, in a 240-hour shaking test of the dispersion, it is possible for the growth rate of the median particle diameter to be about 50% or less. Here, said

shaking test involves the following: 20 ml of slurry is placed into a 50-ml centrifugation tube and set in a vertical shaker; the test starts at a shaking speed of 300 spm and a shaking stroke of 40 mm, and after running it for 240 hours, the centrifugation tube is removed, and the dispersion's median particle diameter is measured and compared to that before the shaking.

[0014] ④ After said intermediate aqueous dispersion has been added into the basic liquid, it can be passed through a filter with a mesh size of 300  $\mu\text{m}$  or less.

[0015] With such constitution, the advantage is that it is possible to remove what is referred to as the coarse particles, which are the particles that were not fully dispersed in the slurry and condensation particles.

[0016] ⑤ The added fumed silica can have a specific area of about 40 – 30 sq. m/g.

[0017] With such constitution, the advantages are that it is possible to control the size of the silica particles in the silica dispersion obtained in this manner, and adjust the performance (e.g. polishing speed) as a polishing agent.

[0018] ⑥ The following can be used as pH adjusting compounds: hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, etc can be used for adjustment on the acidic side; and ammonium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide, barium hydroxide, magnesium hydroxide, etc. can be used for adjustment on the alkaline side.

[0019] As basic compounds that adjust the pH of fumed silica aqueous dispersion, ammonium hydroxide, sodium hydroxide, potassium hydroxide, a calcium hydroxide, barium hydroxide, magnesium hydroxide, etc. can be used.

[0020]

[Mode of Implementing the Invention] Below, we will explain a practical mode of implementing the invention.

[0021] In this embodiment of the preparation method of fumed silica aqueous dispersion, first, fumed silica is added into a liquid whose pH is about 2 ~ 11 (for example, ultrapure water) while applying shearing force, such as to form an intermediate aqueous dispersion in which said silica concentration is 20 ~ 60 % by weight.

[0022] Then, by adding said intermediate aqueous dispersion into a basic liquid (for example, ammonia solution), it is adjusted such that the resulting silica concentration is 1 ~ 50 % by weight and the pH is about 8 – 12.

[0023] In this preparation method, since the fumed silica intermediate aqueous dispersion is added into a basic liquid, the fumed silica is dispersed in the basic liquid in small amounts, and the silica concentration in basic liquid (it becomes the "receiving matrix") increases gradually from zero; therefore the silica particles in the intermediate aqueous dispersion being added can quickly shift to the alkaline region where the zeta potential turns high and the dispersion state turns stable; the stability can be higher with regard to the condensation of the dispersion.

[0024] Therefore the advantage is that even if the energy is applied continuously, silica particles do not condense as readily as in Prior Art.

[0025] Next, we will explain the constitution of this invention more specifically.

(Preparation of fumed silica aqueous dispersion) 21 kg ultrapure water was supplied into the mixer tank (50 L capacity) and 9 kg fumed silica (with a specific area of 70 sq. m/g) was gradually added while applying shear force to said ultrapure water, producing an intermediate aqueous dispersion with a fumed silica concentration of 30 % by weight.

[0026] Then said resulting intermediate aqueous dispersion was gradually added into an ammonia solution and fumed silica aqueous dispersions were prepared in which final silica concentrations were 12 % by weight, 13 % by weight, 15 % by weight, 18 % by weight, and 25 % by weight with pH of 10 – 11.

(Shaking test) Using the fumed silica aqueous dispersions of said individual concentrations, their condensation stability was evaluated by means of the following shaking test. That is, 20 ml samples of individual fumed silica aqueous dispersions were placed into 50 ml centrifugation tubes and set in a vertical shaker (manufactured by Iwaki Sangyo Co., model name KM Shaker V – DX); the shaking was started at a shaking speed of 300 spm and a shaking stroke of 40 mm.

[0027] After a certain time elapsed since the start of shaking (up to 240 hours) the centrifugation tubes were removed and median particle diameters of individual samples were measured and compared to the particle diameters prior to shaking that were considered to be standard 1. Fig. 1 shows a graph of the relation between the growth rate of the median particle diameter of fumed silica aqueous dispersions and the duration of shaking.

(Results) As shown in the graph of Fig. 1, the lower the fumed silica concentration, the smaller and the more stable the growth rate of the median particle diameter. In particular, in the samples whose silica concentrations were 13 % by weight or less, the growth rate of the median particle diameter was less than 50% even in a 240 hour long shaking test; thus they demonstrated extremely remarkable stability.

[0028] These fumed silica aqueous dispersions can be used, for example, as aqueous dispersions that serve as polishing agents for the semiconductor industry (semiconductor wafer polishing slurry).

[0029]

[Effect of Invention] This invention has the above constitution and has the following effect.

[0030] Since the dispersion's stability with regard to condensation can be increased, it is possible to offer a preparation method of a fumed silica aqueous dispersion in which the silica particles do not condense as readily as in Prior Art, even if energy is continued to be applied continuously.

[Brief Explanation of Figures]

[Fig. 1] is a graph that shows the relation between the growth rate of the median diameter in fumed silica aqueous dispersions and the shaking time.

【図1】

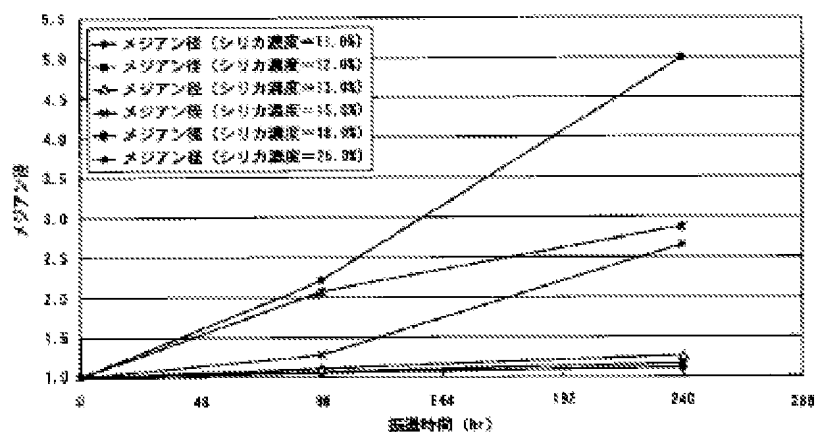


Fig. Shaking test results (Median size)

[Key to Figure]

[Vertical axis] median diameter

[Horizontal axis] shaking time

[Top to bottom in the insert]

Median diameter (silica concentration = 11.0 % by weight)

Median diameter (silica concentration = 12.0 % by weight)

Median diameter (silica concentration = 13.0 % by weight)

Median diameter (silica concentration = 15.0 % by weight)

Median diameter (silica concentration = 18.0 % by weight)

Median diameter (silica concentration = 25.0 % by weight)

United States Patent and Trademark Office

Translations branch

Irina Knizhnik

April 23, 2010